CASTING OF REACTIVE METALS INTO CERAMIC MOLDS

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United States Patent

Feagin

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Related U.S. Application Data

Continuation of Ser. No. 741,661, Jun. 6, 1985, aban-
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Field of Search 252/313.1; 501/152;
106/38.22; 164/12, 20, 516, 518, 519, 34, 521,
529; 428/697

References Cited

U.S. PATENT DOCUMENTS

3,476,691 11/1969 Smith et al. ............... 252/313.1
4,240,828 12/1980 Huseby ..................... 75/135
4,904,591 3/1985 Feagin ..................... 501/105

FOREIGN PATENT DOCUMENTS

1568862 11/1980 United Kingdom

ABSTRACT

The invention concerns a composition for making a coating consisting essentially of a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and mixture of zirconium oxide and yttrium oxide; and a sufficient amount of an yttria sol binder. The composition can be used to prepare refractory materials, casting and core molds.

41 Claims, 4 Drawing Sheets
CASTING OF REACTIVE METALS INTO CERAMIC MOLDS

REFERENCE TO A RELATED APPLICATION

This is a continuation of my copending application Ser. No. 741,661 filed June 6, 1985 now abandoned, which is relied on and incorporated herein by reference.

INTRODUCTION AND BACKGROUND

The present invention relates, in one aspect, to yttria sol used as a binder for a wide variety of refractory materials, casting molds, core molds, related compositions and processes, and casting of reactive metals into ceramic molds. More particularly, the invention pertains to the use of yttria sol as a bonding agent for refractory materials in making the first coat of a ceramic mold for casting of reactive metals such as titanium and titanium alloys. Backup coating compositions may be any of the compatible system known in the art.

Molds produced in accordance with the present invention are particularly useful because they enable the casting of reactive metals with minimized or essentially no alpha case. The present invention results in lower alpha case than is obtainable with conventional molds utilizing other binders previously used in the art. Methods of forming casting molds and core molds are encompassed by the present invention.

In another aspect, the present invention pertains to the use of zirconia sol with selected refractory materials, namely, fused yttrium oxide, or mixtures of fused yttrium oxide and fused zirconium oxide, and the formation of coating compositions therewith and methods of forming molds utilizing same.

For the past 25 years, considerable effort has been devoted to providing capability for casting reactive metals, particularly titanium and its alloys, into ceramic molds. This development and the interest in providing such capability resulted from the interest and activity in the nuclear and aircraft industries where it was necessary to search for high strength and lightweight metals. Since the strength to weight ratio for titanium is very high, use in the aircraft industry was a logical development.

The melting point of titanium metal is almost 3100°F and reacts in the molten condition with most refractories. Earlier attempts to cast titanium into ordinary foundry molds were unsuccessful due to the undesirable chemical reactions between the hot metal and the surfaces with which it came into contact. For example, reduction of the silica produced heavy reaction zones on the casting surface and oxide inclusions. This reaction layer is known in the industry as "alpha case". Problems of alpha case have been described in detail in the literature. Machined and formed graphite molds have been used commercially to make titanium castings. Such molds can be made in such a way as to minimize the alpha case layer. The U.S. Bureau of Mines activities have continued for almost 25 years on the casting of refractory metals. However, there have been continuing efforts for other materials and methods to reduce or eliminate alpha case.

The use of graphite in investment molds has been described in the art in such patents as U.S. Pat. Nos. 3,241,200; 3,243,733; 3,256,574; 3,266,106; 3,296,666 and 3,321,005 all to Lirones. Other prior art which show a carbonaceous mold surface utilizing graphite powders and finely divided inorganic powders called "stuccos" are Operhall, U.S. Pat. No. 3,257,692; Zusman et al., U.S. Pat. No. 3,485,288 and Morozov et al., U.S. Pat. No. 3,389,743. These documents describe various ways of obtaining a carbonaceous mold surface by incorporating graphite powders and stuccos, various organic and inorganic binder systems such as colloidal silica, colloidal graphite, synthetic resin which are intended to reduce to carbon during burnout, and carbon coated refractory mold surfaces. These systems are observed to have the disadvantage of the necessity for eliminating oxygen during burnout, a limitation on the mold temperature and a titanium carbon reaction zone formed on the casting surface.

Further developments including variations in foundry molds are shown in Turner et al., U.S. Pat. No. 3,802,902 which uses sodium silicate bonded graphite and/or olivine which was then coated with a relatively non-reactive coating such as alumina. However, this system still did not produce a casting surface free of contamination.

Schneider, U.S. Pat. No. 3,815,658 molds which are less reactive to steels and steel alloys containing high chromium, titanium and aluminum contents in which a manganesium oxide-forsterite composition is used as the mold surface.

A number of attempts have been made in the past to coat the graphite and the ceramic molds with materials which would not react with the reactive metals being casted. For example, metallic powders such as tantalum, molybdenum, columbium, tungsten, and also thorium oxide had been used as non-reactive mold surfaces with some type of oxide bond. See Brown, U.S. Pat. Nos. 3,422,880; 3,537,949 and 3,994,346.

Operhall, U.S. Pat. No. 2,806,271 shows coating a pattern material with a continuous layer of the metal to be cast, backed up with a high heat conductivity metal layer and investing in mold material.

Basche, U.S. Pat. No. 4,135,030 shows impregnation of a standard ceramic shell mold with a tungsten compound and firing in a reducing atmosphere such as hydrogen to convert the tungsten compound to metallic tungsten or tungsten oxides. These molds are said to be less reactive to molten titanium but they still have the oxide problems associated with them.

Brown, U.S. Pat. No. 4,057,433 discloses the use of fluorides and oxyfluorides of the metals of Group IIIa and the lanthanide and actinide series of Group IIIb of the Periodic Chart as constituents of the mold surface to minimize reaction with molten titanium. This reference also shows incorporation of metal particles of one or more refractory metal powders as a heat sink material. However, even those procedures have resulted in some alpha case problems.

A development by General Electric has provided barrier layers of refractory oxide in a silica bonded mold for casting alloys containing significant amounts of reactive metals; see Gigliotti et al. U.S. Pat. Nos. 3,955,616; 3,972,367 and 4,031,945.

Huseby, U.S. Pat. No. 4,240,828 shows casting a super alloy (containing nickel and cobalt) material containing reactive metals into a ceramic mold containing a rare earth dopant in the alloy.

In the 1960's, developments at Wright Air Development Center led to the formation of a crucible for melting titanium formed from a titanium enriched zirconium oxide crucible with less reaction to molten titanium than pure zirconium oxide.
Richerson, U.S. Pat. No. 4,040,845 shows a ceramic composition for crucibles and molds containing a major amount of yttrium oxide and a minor amount of a heavy rare earth mixed oxide. Such methods including the making of a titanium metal enriched yttrium oxide were only partially successful because of the elaborate expensive and time consuming process which required repetitive steps. Molds for casting molybdenum made from zirconium acetate bonded calcia stabilized zirconia oxide have been made by the Bureau of Mines. p Feagin, U.S. Pat. No. 4,415,673 has reported on the zirconia binder which is an aqueous acidic zirconia sol used as a bond for an active refractory including stabilized zirconia oxide thereby causing reaction and gelation of the sols. Solid molds were made for casting depleted uranium. A distinction is made in this patent between "active" refractories and refractories which are relatively inert. The compositions of Feagin are intended to contain at least a portion of active refractories. See also Feagin, U.S. Pat. 4,504,591.

In summary, the following are four of the processes used for the production of molds for titanium casting and can be set forth as follows:

1. Graphite mold coated with a tungsten powder and a silica binder.
2. A silica binder prepared either from ethyl silicate, aqueous colloidal silica or the like, used to bond thorium oxide for a first coating on a wax pattern. This is then backed up with silica bonded lower cost refractory coatings and stuccos to complete the mold.
3. A zirconium acetate bonded zirconia refractory is used for a first coating. Setting or gelling taken place immediately after application in an atmosphere of ammonia. After drying, this is backed up with a lower cost silica bonded refractory coating to complete the shell mold.
4. A colloidal silica bonded stabilized zirconium oxide (ZrO₂) refractory is used to form the first coat of a mold and this is backed up with a lower cost silica bonded refractory coating to complete the shell mold.

It is generally recognized in the industry that all commercial processes have some alpha case on their casting. This may range from about 0.005 inches to 0.04 inches in thickness depending on process and casting size. The alpha case must be milled off by chemical means or other means from the casting before a satisfactory casting is obtained. The extra cost imposed by the chemical milling operation is a disadvantage and presents a serious problem from the standpoint of accuracy of dimensions. Normally, the tooling must take into consideration the chemical milling which results in the removal of some of the material in order to produce a casting that is dimensionally correct. However, since casting conditions vary, the alpha case will vary along the surface of the casting. This means that there is a considerable problem with regard to dimensional variation.

SUMMARY OF THE INVENTION

The present invention pertains to yttriaia sols and the use of these materials as binders for refractories, and particularly zirconium oxide and/or yttrium oxide, or blends thereof, or fused zirconium oxide and/or fused yttrium oxide or blends thereof as a refractory component in making a mold coating composition consisting essentially of those ingredients. The invention further relates to the reactive compositions of the sols and the refractory material and the mold coatings and cast shapes prepared therefrom. The invention also pertains to the method of making the coating compositions and methods of making molds. Of particular interest is the method of making a mold coating compositions and methods of making molds. Of particular interest is the method of casting titanium and titanium alloys such as Ti₆Al₁₄V and the reduction of alpha case which is brought about by the present invention.

In a further aspect of the invention, the invention pertains particularly to coatings and molds for metal casting, and to the use of yttria sol as a binder for a variety of refractories, metal powders, and fibers for various application.

Still further, the invention includes within its ambit the use of zirconia sol with a selected group of refractory substances, the formation of coating compositions therefrom and the production of casting surfaces therefrom.

An object of the invention is to provide a composition suitable for making a mold coating which is less reactive with titanium and titanium alloys during casting.

Another object of the invention is to provide a low reactivity mold coating for reactive metal casting.

A further object of the invention is to provide a ceramic mold having a casting surface having low reactivity with reactive metals.

Yet another object of the invention is to provide a castable refractory composition, using yttria sol as the binder, and the resulting ceramic body.

Finally, it is a further object of the present invention to provide certain compositions and processes utilizing zirconia sols and to obtain novel product therefrom.

By the term "reactive metals" is meant those metals and alloys which may react with or produce a relatively rough mold surface when poured into ordinary investment casting molds having mold surfaces containing one or more of the following refractories: silica, alumina, aluminosilicates, zirconium silicate (zircon) or other oxides and mixed oxides normally used in investment casting molds. Examples of these reactive metals are titanium, titanium alloys such as Ti₆Al₁₄V, zirconium, zirconium alloys, high carbon steels, eutectic alloys (containing appreciable amounts of tungsten, hafnium, carbon, nickel, cobalt, etc.), aluminum-lithium alloys, nickel base alloys containing appreciable amounts of titanium or aluminum or hafnium or tungsten. One of the most reactive of all the metals is titanium. These terms are fully discussed in Feagin, U.S. Pat. Nos. 4,415,673 and 4,504,591 which are incorporated herein by reference.

It is therefore a feature of the invention to provide a refractory composition comprising yttria sol and any compatible finely divided, hardenable refractory binder substance. In particular, these compositions are coating compositions comprising a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, and/or sodium silicate.
oxide, fused yttrium oxide, fused zirconium oxide, monoclinic zirconium oxide, yttrium oxide, cubic zirconium oxide, fused stabilized zirconium oxide having as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other rare earth oxides, blends of zirconium and yttrium oxides or with other constituents in this group, and fused blends of zirconium and/or yttrium oxide with other rare earth oxides, and mixtures of any of the above, and a sufficient amount of a yttria sol binder.

In a further aspect, the invention resides in a process for making an investment casting mold having low reactivity with reactive metals comprising providing a yttria sol, mixing said sol with any of the above-mentioned refractory materials, including but not limited to yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide and mixtures thereof, to form a coating composition, applying said coating composition to a pattern shaped in the desired configuration, heating the resulting coated pattern to a sufficiently high temperature to melt or burn out the pattern material, and thereby sintering said coating composition into the desired shape.

Among the suitable refractory materials are monoclinic zirconium oxide, yttrium oxide, cubic zirconium oxide, fused stabilized zirconium oxide having as the stabilizing agent from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other rare earth oxides, blends of zirconium and yttrium oxides or with other constituents in this group, and fused blends of zirconium and/or yttrium oxide with other rare earth oxides.

A still further feature of the invention resides in a process for making a ceramic core comprising coating the inside of a core mold with a slurry comprising yttria sol and any of the above-mentioned refractory materials, including but not limited to yttrium oxide, zirconium oxide, fused yttrium oxide and a mixture of fused yttrium oxide and zirconium oxide, and other, before the coating is dry applying thereto finely divided refractory and permitting the coating to dry, thereafter applying to the coating a mixture of a refractory and a binder thereof removing the core from the mold and firing said core at a sufficiently high temperature to bond the coating and the silica refractory.

Also, a further feature of the invention resides in a process for casting a reactive metal in a mold having low reactivity with reactive metals comprising providing a yttria sol, mixing said sol with a refractory material to form a coating composition, applying said coating composition to a pattern shaped in the desired configuration, allowing the coating to gel, heating the resulting coated pattern to a sufficiently high temperature to melt or burn out the pattern material, thereby fusing said coating composition into the desired shape, thereafter casting said metal into the mold.

It is a further feature of the invention to provide refractory compositions comprising zirconia sol and a refractory selected from the group consisting of fused yttrium oxide, fused zirconium oxide and mixtures thereof.

In a further aspect, the invention resides in a process for making an investment casting mold having low reactivity with reactive metals comprising providing a zirconia sol, mixing said sol with a refractory material related from the group consisting of fused yttrium oxide, fused zirconium oxide and mixtures thereof, to form a coating composition, applying said coating composition to a pattern shaped in the desired configuration, heating the resulting coated pattern to a sufficiently high temperature to melt or burn out the pattern material, and thereby sintering said coating composition into the desired shape.

A still further feature of the invention resides in a process for making a ceramic core comprising coating the inside of a core mold with a slurry comprising zirconia sol and a refractory material selected from the group consisting of fused yttrium oxide, fused zirconium oxide and a mixture of fused yttrium oxide and fused zirconium oxide, and before the coating is dry applying thereto finely divided refractory and permitting the coating to dry, thereafter applying to the coating a mixture of a refractory and a binder thereof and permitting this mixture to gel to form a core, thereafter removing the core from the mold and firing said core at a sufficiently high temperature to bond the coating and the silica refractory.

DETAILED DESCRIPTION OF THE INVENTION

The binders used for the experiments described herein were aqueous, although non-aqueous sols can be used. Organic solvents, for example an alcohol, may be utilized but these are much more difficult to produce and are necessarily more costly.

The yttria sol used in these experiments has a pH of approximately 6.5–7.0 and a concentration of preferably 14% Y₂O₃, although this can vary as well as the pH.

TYPICAL PHYSICAL AND CHEMICAL PROPERTIES

<table>
<thead>
<tr>
<th>Yttria Sol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TABLE 1</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Color</strong></th>
<th>almost colorless, transparent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH, 25°C</strong></td>
<td>6.5–7.0</td>
</tr>
<tr>
<td><strong>Particle Size, µm</strong></td>
<td>10</td>
</tr>
<tr>
<td><strong>Particle Charge</strong></td>
<td>Positive</td>
</tr>
<tr>
<td><strong>Specific Gravity, 25°C</strong></td>
<td>1.17</td>
</tr>
<tr>
<td><strong>Weight %, yttrium oxide</strong></td>
<td>14</td>
</tr>
<tr>
<td><strong>Viscosity, cps</strong></td>
<td>10</td>
</tr>
<tr>
<td><strong>Shelf life</strong></td>
<td>At least six months</td>
</tr>
<tr>
<td><strong>Dilute with water</strong></td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Subject to freezing</strong></td>
<td>Freeze-Thaw Stable</td>
</tr>
</tbody>
</table>

The zirconia sol used in the work reported herein was from various lots containing approximately 20% ZrO₂ and having a pH of approximately 3–3.7 and was acetate stabilized. However, other types of zirconia sols may be used such as nitrate stabilized sols. Other stabilized sols in lower pH ranges may also be used even as low as 0.5 pH. It is more desirable to use a low reactivity stabilizer and a pH higher than 3 to minimize the safety hazard of handling the more acidic material.

The following table shows the physical properties of the zirconia sol. The color is very slightly amber for both sols shown on the table. The pH is quite different which the acetate stabilized being at about 3.6–4 and the nitrate stabilized being at less than 2. The specific gravity is different in the two types because of the stabilizing ions. The particle size of the zirconia particle is in the range of about 20 Angstroms 0.002 micron. The zirconia particles have a positive charge. The viscosity is low, with the composition being slightly thicker than water. Although the sol will freeze, they are freeze-thaw stable.
Table 2 shows the chemical properties of the zirconia sols. A typical ZrO2 content is 20% in each case. Due to the fact that hafnia is generally present in most commercial zirconia, it is present in approximately 0.4% in the sol used for purposes of this invention. However, it is not considered an essential ingredient. The sodium content is approximately 0.04% and approximately 0.05% iron. Calcium plus magnesium is less than 0.04%. As noted, the stabilizing ion in both products is $\pm 0.2$ mole of stabilizing ion per mole of ZrO2. This varies slightly depending upon the exact pH and the exact percent ZrO2. Shelf life of these products is over one year and they can be diluted with water to any concentration desired. These sols will gel or precipitate ZrO2 upon addition of alkalis or multivalent ions such as sulfate or phosphate.

In general, concentrations of the oxides in the sols can be varied higher or lower depending upon other factors in the process such as composition of the coating, type of refractory used, particle size of the refractory and mold firing conditions.

For purposes of the present invention, refractory powders or aggregate suitable for use in the mold coatings or for the casting surface of a mold or for a melting crucible are those of the following group: monoclinic zirconium oxide, yttrium oxide, cubic zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide having as the stabilizing agent a member from the group of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide and other rare earth oxides, blends of zirconium and yttrium oxides or with other constituents in this group and fused blends of zirconium and/or yttrium oxide with other rare earth oxides.

These may be used with the ytria sols, or mixtures of one or more thereof may be used. When zirconia sol is used, either fused yttrium oxide or fused zirconia oxide a mixture of fused yttrium oxide and fused zirconium oxide may be used.

It has been found that zirconium oxide or calcium or magnesium oxide stabilized (2.0-4.0 % CaO or MgO) zirconium oxide mixed with zirconia sol as the binder and used as the first coating of an investment cast shell mold, produces a alpha case of approximately 0.020-0.025" thick using a Ti6A14V alloy poured into a mold at 1000°F. Mold surfaces using fused mixtures of zirconium and yttrium oxides had lower alpha case, and a mold surface comprising a high content of yttrium oxide showed very low alpha case.

In preparing molds for casting in Ti6A14V alloy a number of pattern wax bars approximately $\frac{3}{8}$" diameter were cut into lengths (fingers) about 5" long. The first coating to form the mold surface was applied to a 4" portion of this finger, leaving about one inch uncoated. The application of the coating was by dipping the finger into the slurry or spraying the coating on to the wax finger. While it was still wet, the stucco was applied. The coated finger was then allowed to dry. After all, the wax fingers were coated, stuccoed and dried, they were attached by wax sealing the uncoated end to a wax pouring funnel about 4" diameter and 4" high with a flat base at the small end. Four or five fingers were attached to each funnel.

After sealing the wax fingers to the funnel, the exposed wax surface of each finger and funnel was coated in an experiment V for facecoat (essentially 99% Y2O3 when dried) and while wet immediately after coating it was stuccoed with $40+100$ mesh fused Y2O3. This was then allowed to dry.

The first coat applied to the wax finger is called the facecoat and the slurry compositions thereof are given in Tables 3 and 4 along with their viscosity readings during application of the coating, and the type of stucco refractory used on each finger experiment.
In each of the facecoats a small amount of an acrylic vinyl latex was added to the slurry to aid in continuous film formation, better adhesion to the wax bar, and to prevent possible penetration of the silica binder to the mold surface during dipping of the backup coats. Several types of latex can be used if compatible with the slurry.

Finger samples H-2 and V-2 had two duplicate firstcoats of slurry-stucco 405 and 405 respectively instead of one first coat (primary coat) for the other fingers.

The entire mold assemblies were then dipped into Slurry 417 and immediately stucced with Remasil 60 stucco, 70 mesh grain size. This coating was allowed to harden and recoated with the same slurry, stuccoing with a 50 mesh grain size. This was repeated until a total of seven coats had been applied to the wax pattern. The last coating was not stucced. After all coats were applied, the molds were allowed to dry thoroughly for several days before dewaxing, although a long dry time is not essential.

The molds were dewaxed in hot pure motor oil at about 130° C, and then preheated to 2500 F. to adequately mold the surface and allowed to cool until ready for casting.

The refractories and other materials used in preparing the slurries used in accordance with the invention are described as follows:

1. Vinyl-acrylic latex, a commercial product available from several sources; e.g. Air Products Co., used to provide improved film forming properties to the slurry and to prevent penetration of liquids from subsequent coats to the mold surface.
2. Sterox NJ a product of Monsanto Chemical Co. and is a low-foaming wetting agent.
3. 2-ethyl hexanol, a commercial chemical, used as a defoaming agent.
4. Zirconia sol, transparent in appearance, acetate stabilized, containing approximately 20% ZrO₂, pH 3.2, sold by Remet Corporation.
5. Yttria sol, containing approximately 14% Y₂O₃, pH approximately 7, transparent in appearance, sold by Remet Corporation.
6. Glacial acetic acid, a standard commercial product.
As to alpha case measurements, the samples cast at 1000° F. mold temperature were measured accurately. This would represent the worst reaction condition. Looking at Table 5, there is very little difference in the spread of the alpha case on samples I, G, K, F, T, X. There appears to be more uniformity in sample W. Sample U on mold 2 appears to have potentially half the case in some areas than the other samples. Sample H on mold 1 with yttria as the major surface constituent is very low in alpha case being less than 0.001". Sample V on mold 2 having greater than 99% yttria as the mold surface was the best at 0.0001". The isolated 0.007" case point is probably related to the inconsistency of the process used in making the surface.

On Table 6, one notes samples V and V2 on mold 3 with slight variations in the process, having less than 0.0001" case. Sample V, mold 4, was very low in case but contained an isolated high spot attributed to process defect. Samples H and H2 with similar slight process variations also confirm previously low figures on mold 1. Samples BB and CC on mold 3 which contain some silica in the mold surface have approximately the same amount of case as some of the other experimental samples. On mold 4, there is a reconfirmation of results obtained on mold 1. In comparing depth of alpha case on 500° F. vs 1000° F. molds in general, the depth was less on the 500° F. and less intense. Samples H and V were essentially free of alpha case at both temperatures. Sample U was considerably lower on alpha case than the average.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**FIG. 1** is a photomicrograph of a cut section of a molded metal article exhibiting alpha case.

**FIG. 2** is a photomicrograph of a cut section of a molded metal article exhibiting less alpha case than in **FIG. 1**.

**FIG. 3** shows representative alpha case on Sample G at 500° F. mold 1. All remaining photomicrographs are at 75X.

**FIG. 4** shows lack of case on Sample H at 500° F. mold 1.

**FIG. 5** shows the case on Sample T at 500° F. mold 2. For comparison, **FIG. 6** shows the case on Sample T at 1000° F. mold 2, indicating thicker and more pronounced case.

**FIG. 7** shows the case of Sample X at 500° F. mold 2.

**FIG. 8** is a photomicrograph of Sample U at 1000° F. mold 2. There is an isolated spot of alpha case and a large area without any case on the sample.

**FIG. 9** shows the relatively faint alpha case area on Sample CC, mold 3 at 500° F. mold temperature. This contrasts with a more pronounced and wider case area on the same sample at a mold temperature of 1000° F., **FIG. 10**.

**FIG. 11** shows no case on Sample V, mold 3 at 500° F. mold temperature. Similarly, **FIG. 12** shows no case on Sample V2, mold 3, at 500° F. mold temperature.

From the above photomicrographs it appears that a casting mold surface having a major yttrium oxide content has considerably less reaction with titanium cast into such mold, producing extremely low alpha case.

Individual blends of yttria sol were made with the following refractories; fused silica, zirconia and graphite, alumina, silicon carbide. All of these are classified in the art as being relatively "inactive refractories". The compositional details are set forth below: The yttria sol composition was about 14% Y2O3 at a pH of about 7 in water.

Relative to the proportions of refractory to be used with the yttria sol, in the case of relatively "inactive" refractories such as monolithic zirconia, tabular alumina, fused silica and zircon, these can vary widely depending upon their particle size distributions, the specific gravity of the refractory, the manner of processing such as injection molding, casting, pressing or dipping, and the application of the mix. In general, when slurries are made for dipping investment casting patterns with fused silica refractory flour of about 325 mesh, a ratio of one part flour to one part yttria sol is about the minimum. As much as two parts of refractory can be used to produce a thick slurry coat. A range of about two to five parts of monolithic zirconia can be used. In the case of zircon and tabular alumina of similar particle size distributions a range of about two to four parts of flour to one part sol can be used. Variations in these proportions may be made depending upon the particular results desired. Other processes, such as injection molding, casting, etc. would require less sol with the refractory. Dry pressing would require still less sol to provide proper pressing consistency.

In the case of using "active" refractories with yttria sol, such as yttria-stabilized zirconia, fused yttrium oxide, fused yttria-zirconia, blends of yttrium oxide with other refractories, somewhat more sol may be required to prolong shelf life of the mix. Some of these refractories will "gel" the sol but by controlling the proportions the mixes may be processed satisfactorily before gelation. The ultimate gelation and hardening of the mix is advantageous in making refractory shapes.

It is further advantageous to bond refractory fibers with yttria sol to produce high refractories. Such fibers include silicon carbide, silicon nitride, carbon fibers, alumina fibers and the like.

Many of the compositions produced from the yttria sol-refractory fiber system may be used for special coatings and for casting shapes when a gelling agent or active refractory is used with the yttria sol.

The separate slurries made with yttria sol and zircon, alumina and fused silica were deposited on a wax pattern and allowed to dry. The resulting coating was strong and resisted scrapping with a knife. Protective coating may be applied to many types of surfaces such as ceramics, metals, foundry molds, and for electronic applications. For example, an yttria sol-fused yttria refractory powder slurry can be used to spray paint or coat a refractory melting crucible to minimize metal crucible reaction. It may also coat a pouring basin or...
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A ceramic core suitable for reactive metal casting and particularly titanium can be made by making an yttria sol- yttria type refractory or other and casting or injection molding or pressing into a suitable mold and allowing the sol to gel. The gelled body can then be dried and fired and used as a casting core.

It has been found that yttria sol and zirconia sol are compatible. Therefore, it is possible to use a homogeneous blend of these two sols if desired rather than either sol alone.

Further variations and modifications will be apparent to those skilled in the art from a reading of the foregoing and are intended to be encompassed by the claims appended hereto.

I claim:

1. A composition for making a coating consisting essentially of a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and fused mixtures of zirconium oxide and yttrium oxide; and a sufficient amount of an yttria sol binder.

2. The composition as set forth in claim 1, wherein the sol is aqueous.

3. The composition as set forth in claim 1, wherein the zirconium oxide is monoclinic or cubic in structure.

4. The composition as set forth in claim 1, wherein the fused stabilized zirconium oxide has as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element; said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.

5. The composition as set forth in claim 1, wherein said yttria sol is about 14% Y₂O₃ with a pH of 6.5–7.0.

6. The process of making a coating according to claim 1, consisting essentially of mixing yttria sol with a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and fused mixtures of zirconium oxide and yttrium oxide.

7. The process as set forth in claim 6, wherein the zirconium oxide is monoclinic or cubic, and the fused stabilized zirconium oxide has as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element, said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.

8. The process as set forth in claim 6, wherein said yttria sol is about 14% Y₂O₃ with a pH of 6.5–7.0.

9. The process of coating a foundry mold with a coating comprising, the foundry mold material being reactive with reactive metals and alloys, comprising applying to at least the surfaces of said foundry mold which come into contact with said reactive metals or alloys, a composition consisting essentially of a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and fused mixtures of zirconium oxide and yttrium oxide; and a sufficient amount of an yttria sol binder.

10. The process as set forth in claim 9, wherein the sol used in the process is aqueous.
11. The process as set forth in claim 9, wherein the zirconium oxide is monoclinc or cubic.

12. The process as set forth in claim 9, wherein the fused stabilized zirconium oxide has as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element; said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.

13. The process as set forth in claim 9, wherein said yttria sol is about 14% Y₂O₃ with a pH of 6.5-7.0.

14. A shaped surface having a coating thereon made from a composition according to claim 1, consisting essentially of a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and mixedtures of zirconium oxide and yttrium oxide; and a sufficient amount of an yttria sol binder.

15. The shaped surface as set forth in claim 14, wherein the zirconium oxide is monoclinc or cubic.

16. The shaped surface as set forth in claim 14, wherein the fused stabilized zirconium oxide has as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element, said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.

17. The shaped surface as set forth in claim 14, wherein said yttria sol is about 14% Y₂O₃ with a pH of 6.5-7.0.

18. A shaped mold having the configuration of a desired molded article made from a composition according to claim 1 consisting essentially of a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and mixedtures of zirconium oxide and yttrium oxide; and a sufficient amount of an yttria sol as a binder.

19. The mold as set forth in claim 18, wherein the zirconium oxide is monoclinc or cubic.

20. The mold as set forth in claim 18, wherein the fused stabilized zirconium oxide has as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element, said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.

21. The mold as set forth in claim 18, wherein said yttria sol is about 14% Y₂O₃ with a pH of 6.5-7.0.

22. A cast ceramic core having a configuration around which the metal is cast to form the desired molded article, said core consisting essentially of a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and mixedtures of zirconium oxide and yttrium oxide; and a sufficient amount of an yttria sol as a binder.

23. The cast ceramic cord as set forth in claim 22, wherein the zirconium oxide is monoclinc or cubic.

24. The cast ceramic core as set forth in claim 22, wherein the fused stabilized zirconium oxide has as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element, said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.

25. The mold as set forth in claim 21, wherein said yttria sol is about 14% Y₂O₃ with a pH of 6.5-7.0.

26. A process for making a refractory article having low reactivity with reactive metals consisting essentially of providing an yttria sol, mixing said sol with a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and mixedtures of zirconium oxide and yttrium oxide to form a coating composition, applying at least one coating of said coating composition to a surface object shaped in the desired configuration, heating the resulting coated surface object to a sufficiently high temperature to melt or burn out the material of the surface object, thereby sintering said coating composition into the desired shape.

27. The process according to claim 26, wherein multiple coatings of said composition are applied to said surface object until a coating of the desired thickness is built up and thereafter heating the thin coated surface object to melt and burn out the surface object material and then hardening the resulting refractory article.

28. The process as set forth in claim 26, wherein the zirconium oxide is monoclinc or cubic.

29. The process as set forth in claim 26, wherein fused stabilized zirconium oxide has as the stabilizing agent a member selected from the group consisting of calcium oxide, magnesium oxide, yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element; said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.

30. The process as set forth in claim 26, wherein said yttria sol is about 14% Y₂O₃ with a pH of 6.5-7.0.

31. The process according to claim 26, wherein there is applied to the exterior of the resulting sintered coating a refractory material to build up a refractory mold.

32. The process according to claim 26, wherein a plurality of coatings of refractory material are applied.

33. The process according to claim 26, wherein the surface shaped body is a pattern.

34. The process according to claim 26, wherein the surface shaped body is shaped in the form of a core.

35. A process for making a refractory article having low reactivity with reactive metals consisting essentially of providing an yttria sol, mixing said sol with a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and mixedtures of zirconium oxide and yttrium oxide; to form a coating composition, applying a first coating of said coating composition to a surface body shaped in the desired configuration, and thereafter applying at least one second coating of a refractory to said surface body having the first coating thereon, heating the resulting coated body to a sufficiently high temperature to melt or burn out the body material, thereby sintering said coating composition into the desired shape.

36. The process according to claim 35, wherein said second coating is a composition different from the said first coating.

37. The process according to claim 35, wherein said second coating is a composition comprising an yttria sol and a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, lanthanum oxide, dysprosium oxide, and other oxides of a rare earth element; said rare earth element being a member of the Periodic Table of elements with an atomic number from 57 to 71.
oxide, fused zirconium oxide, fused stabilized zirconium oxide and fused mixtures zirconium oxide and yttrium oxide.

38. A process for making a ceramic core comprising coating the inside of a core mold with a slurry consisting essentially of yttria sol and a refractory material, and before the coating is dry, applying thereto finely divided refractory and permitting the coating to dry, thereafter applying to the coating a mixture of a refractory and a binder thereof and permitting this mixture to gel to form a core, thereafter removing the core from the mold and firing said core at a sufficiently high temperature to bond the coating and the silica refractory.

39. A process for casting a reactive metal in a mold having low reactivity with reactive metals consisting essentially of providing a yttria sol, mixing said sol with a refractory material to form a coating composition, applying said coating composition to a pattern shaped in the desired configuration, allowing the coating to gel, heating the resulting coated pattern to a sufficiently high temperature to melt or burn out the pattern material, thereby sintering said coating composition into the desired shape, thereafter casting said metal size into the mold.

40. The process according to claim 39, wherein there is applied to the exterior of the resulting sintered coating a refractory material to build up a refractory mold.

41. A process for making a ceramic core as set forth in claim 38 comprising coating the inside of a core mold with a slurry consisting essentially of yttria sol and a refractory material selected from the group consisting of yttrium oxide, zirconium oxide, fused yttrium oxide, fused zirconium oxide, fused stabilized zirconium oxide, and fused mixtures of zirconium oxide and yttrium oxide, before the coating is dry, applying thereto at least one coating of finely divided refractory and permitting the coating to dry, thereafter applying to the coating at least one coating of a mixture of a refractory and a binder thereof, removing the core from the mold and firing said core at a sufficiently high temperature to bond the coating and the silica refractory.

* * * * *
It is certified that an error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In column 1, in line 46, after "and", insert --it--;

In column 3, in line 10, delete "p", in that same line, a new paragraph should being with the word "Feagin";

In column 3, in line 32, change "taken" to --takes--;

In column 3, in line 59, change "yttriaia" to --yttria--;

In column 5, in line 46, delete "silica";

In column 6, in line 20, delete "silica";

In column 10, in line 32, change "8." to --8,--;

In column 10, in line 35, change "11. but -500" to --11, but -50--;

In column 10, in line 36, change "16." to --16,--;

In column 12, in line 63, change "surfaes" to --surfaces--;
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

IN THE CLAIMS:

Column 15, claim 20, line 3, after "agent" insert "a--";
Column 15, claim 23, line 1, change "cord" to "core--";
Column 17, claim 38, line 13, delete "silica";
Column 17, claim 39, line 17, change "sold" to "sol--"; and
Column 18, claim 41, line 21, delete "silica".

Signed and Sealed this
Fourteenth Day of January, 1992

Attest:

HARRY F. MANBECK, JR.
Attesting Officer
Commissioner of Patents and Trademarks